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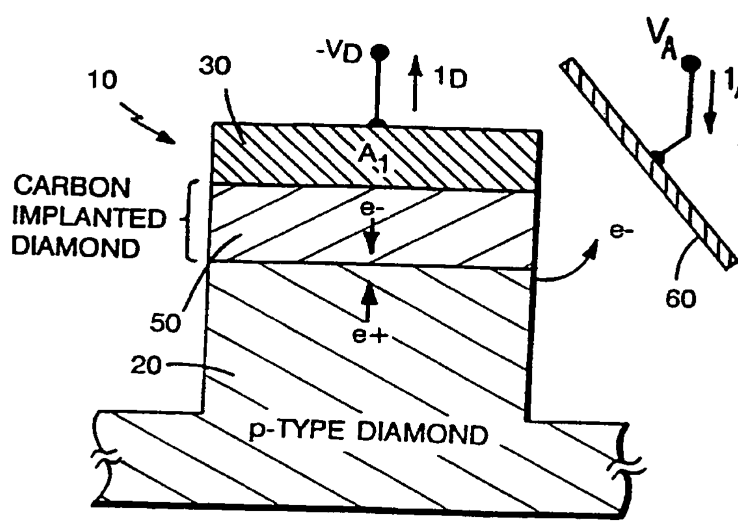


(57) Abstract

A cold cathode device is provided comprising a wide-bandgap (> 5 eV) material exhibiting negative electron affinities, low trap densities, and high carrier mobilities, a junction between a first region (50) of the wide-bandgap material having n-type conductivity and a second region (20) of the wide-bandgap material having p-type conductivity, and a conductive contact (30) to forward bias the junction causing electrons to be emitted near the junction into an exterior region.

DIAMOND COLD CATHODE

The invention relates to cold cathodes for emitting electrons into a vacuum.

Robust, high-current-density (>1000 A cm^{-2}) cathodes while difficult to make are desirable for application in high-power, high-frequency devices.

A first prior art approach for fabricating these cathodes uses high electric fields produced at sharp edges or tips to cause electrons to tunnel out of a metal into vacuum (as described by Spindt et al., "Field-emission arrays for vacuum microelectronics," in *Proc. 3rd Int. Conf. Vacuum Microelectronics*, C.A. Spindt and H.F. Gray, Eds., New York: IEEE, 1991; Thomas et al., "Fabrication and some applications of large-area silicon field emission arrays," *Solid-State Electron.*, vol. 17, pp. 155-163, 1974; and Gray et al., "A silicon field emitted array planar vacuum FET fabricated with microfabrication techniques," in *Science and Technology of Microfabrication*, R.E. Howard, E.L. Hu, S. Namba, and S.W. Pang, Eds., Pittsburg, PA: Materials Research Society, 1987, pp. 23-30). However, as noted by Spindt et al., at high current densities these electric-field-assisted cathodes are unreliable and prone to catastrophic failure.

A second approach for fabricating these cathodes uses conventional semiconductors, such as Si (as in Martinelli et al., "The application of semiconductors with negative electron affinity surface to electron emission devices," *Proc. IEEE*, vol. 62, pp. 1339-1360, 1974), GaAs (as in Scheer et al., "GaAs-Cs: A new type of photoemitter," *Solid State Commun.*, vol. 3, pp. 189-193, 1965), or some organic crown ethers (as in Dye, "Electrides: Ionic salts with electrons as the anions,"

"Synthesis of n-type semiconducting diamond film using diphosphorus pentoxide as the doping source," in *Appl. Phys. A*, vol. 51, pp. 1731-1733, 1991; and Geis, "Growth of device-quality homoepitaxial diamond thin films," in *Diamond, SiC, and Related Wide Bandgap Semiconductors*, vol. 162, J.T. Glass, R. Messier, and N. Fujimori, Eds., Pittsburg, PA: Material Research Society, 1990, pp. 15-22) and grown with sufficient quality to have low trap densities and high carrier mobilities, making it a semiconductor instead of an insulator, as noted by Geis.

Reference is also made to a paper of Bajic and Latham entitled "Enhanced cold-cathode emission using composite resin-carbon coatings" in J.Phys. D: appl. Phys. 21 (1988) 200-204 and a paper of Geis, Smith, Argoitia, Angus, Ma, Glass, Butler, Robinson and Pryor entitled "Large-area mosaic diamond films approaching single-crystal quality" in Appl. Phys. Lett. 58 (22), 3 June 1991, 2485-87.

The present invention provides cold cathodes that are not adversely effected by standard semiconductor processing and do not have catastrophic failures. Therefore, devices embodying the invention can be used as cathodes in useful micron-sized, high-power, high-frequency vacuum devices. Devices embodying the invention may be used in place of conventional high-power vacuum tubes, pressure gauges, and other systems where hot filaments traditionally are used to generate free electrons.

In general, in one aspect, the invention features a cold cathode device, and a method for making the same, comprising a wide-bandgap (>5 eV) material exhibiting negative electron affinities, low trap densities, and high carrier mobilities, a junction between a first region of the wide-bandgap material having n-type conductivity and a second region of the wide-bandgap

A feature includes a cold cathode by electron emission from n-type semiconductor (diamond) with electric fields less than 10^6 V cm^{-1} (without p-type material or a diode in the semiconductor).

A feature resides in using sharp points etched in the semiconductor (diamond) to increase electron emission at low average electric fields. A feature resides in using ion beam assisted etching to form the sharp points in the diamond.

A feature resides in a cathode where the material is diamond, and more specifically, where the emitting surface is (111)-orientation of diamond.

A feature resides in the formation of n-type diamond using phosphorous doping.

These and other objects, uses, and advantages of the invention will be apparent to those skilled in the art from the following detailed description when read in connection with the accompanying drawings wherein like reference numerals designate like parts and wherein:

FIG. 1 depicts a schematic drawing of a high current density diamond cold cathode;

FIG. 2 depicts a schematic drawing of an experimental diamond cold cathode;

FIG. 3 depicts a graph of the anode current, I_A, as a function of the current to the aluminum contact, I_D, for the cold diamond cathode of FIG. 2; and

FIG. 4 depicts a graph of the anode current, I_A, as a function of the anode voltage V_A, for the cold diamond cathode of FIG. 2.

An exemplary embodiment of the present invention is a diamond cold cathode, indicated generally by **10** in FIG. 1, produced by forming diodes in diamond using carbon ion implantation into heated (320 °C) substrates **25**, as described by Prins, "Bipolar transistor action in ion implanted diamond," *Appl. Phys. Lett.*, vol. 41, pp.

area of the p-type homoepitaxial diamond thin-film region **40** of thickness less than about 1 μm (the minority carrier diffusion length), and ultrahigh-vacuum environments.

An experimental embodiment of the present invention is a diamond cold cathode, indicated generally by **10** in FIG. 2, produced by forming diodes in p-type semiconducting diamond using carbon ion implantation into heated (320 °C) substrates **20**, as described by Prins, "Bipolar transistor action in ion implanted diamond," *Appl. Phys. Lett.*, vol. 41, pp. 950-952, 1982. A current density of 10^{-5} A cm^{-2} is used, with ion energies of 50, 106, or 170 keV and ion fluences of 3.8×10^{16}, 3×10^{16}, or 3.5×10^{16} cm^{-2}, respectively. The substrate **20** is then coated with 1 μm of electron-beam-evaporated Al, patterned into 60x60 μm^2 squares **30** on 100 μm centers using standard photolithography. The resistance between Al squares **30** and to the p-type substrate **20** is in the range of about 10^2 to about 10^3 Ω and is ohmic in character. The coated, patterned substrate is then etched to a depth of 1.1 μm with ion-beam-assisted etching (as in Efremow et al., "Ion-beam-assisted etching of diamond," *J. Vac. Sci. Technol. B*, vol. 3, pp. 416-418, 1985), using the Al squares **30** as a mask to form mesa structures **10** comprising a conductive contact layer of Al **30**, a region of carbon-implanted diamond **50** having n-type conductivity, and a region of substrate **20** having p-type conductivity. After etching, diamond cold cathode structures **10** constructed in this manner exhibit diode character to the p-type substrate **20** with breakdown voltages of 400 to 600 V. The structures **10** are then mounted in either indium or silver-doped epoxy, cleaned in an oxygen plasma, and rinsed in water and acetone.

For measurements of emitted current, the mesa-etched diodes **10** are characterized in a turbopumped

measurements), and in chemical-vapor-deposited homoepitaxial diamond as described in the Geis paper with estimated boron concentrations of 10^{19} cm^{-3}.

Mesa-etched Al-diamond Schottky diodes, fabricated as described hereinabove but without carbon implantation, did not emit current when forward biased to the same voltage and current levels as the implanted diodes **10**.

By varying the substrate temperature from 25 to 100 °C and keeping I_D constant, V_D could be varied from -200 to -100 V. To within experimental error, a factor of 3, I_A is independent of V_D.

Diodes fabricated in insulating, type IIa diamond exhibited no forward or emitted currents when forward biased (V_D = -100 V).

Modified diodes were formed by etching 230 nm into the carbon-implanted substrate, removing the dark conductive layer formed during carbon implantation. Without the conductive layer, the 60x60 μm^2 Al squares formed diodes to the substrate and back-to-back diodes to each other. After the substrate was etched a second time to form mesas, as described hereinabove, the diodes exhibited diode current-voltage characteristics nearly identical to the unmodified diodes **10** and still emitted current when forward biased.

These results indicate that current flow through the diode produces current emission and that Al-diamond Schottky diodes with a barrier height of less than 2 eV do not emit electrons. The dark conductive layer formed during carbon implantation, which is similar to graphite according to Prins, "Electrical resistance of diamond implanted at liquid nitrogen temperature with carbon atoms," *Rad. Effects Lett.*, vol. 76, pp. 79-82, 1983, with a resistivity of about 8×10^{-3} Ω cm and a temperature coefficient of -4×10^{-6} Ω cm °C^{-1}, is not required for current emission. The large forward voltage (about 2 V)

$2x10^{-5}$ and current densities of about $2x10^{-2}$ A cm^{-2} (as in Ea et al., "Array silicon avalanche cathodes," *IEEE Electron Device Lett.*, vol. 1, pp. 403-405, 1990).

The invention has also been used to obtain electron emission from diamond (111) surface by ion implanting the diamond with carbon. The implantation was performed with the substrate at 320° C. using a 50 keV ion beam and a dose of $3.2x10^{16}cm^{-2}$ as described above.

When the sample was initially loaded into the vacuum chamber, there was no emission current from the diamond. However, by moving the anode which is usually about 1mm above the diamond, on the diamond and passing current through the diamond-anode contact, there was emission when the anode was then moved to about a millimeter above the diamond sample. Addition of O_2(~ 1-5 $X10^{-2}$ Torr) to the chamber during emission did improve emission current. However, also adding moist air, by breathing on the diamond, resulted in a substantial increase in emitted current on the order of 1 mA cm^{-2}. After activation with both O_2 and H_2O vapor, there was emission current with an anode voltage as low as 500 V. The electric field was believed to be on the order of $5X10^3$ V cm^{-1} for emission. The current increased with anode voltage showing a space-charge-like current increase with voltage in contrast with an exponential current increase with voltage usually found with conventional field emission cathodes.

It is believed that the electric field for electron emission may be further reduced by patterning the substrate to have a series of sharp points. These points have locally high electric fields causing emission; however, the average electric field is much lower.

Such points may be formed with an etching technique, such as ion beam assisted etching (IBAE), such

Claims

1. A cold cathode device comprising

a wide-bandgap (>5 eV) material exhibiting negative electron affinities, low trap densities, and high carrier mobilities having a first region on n-type conductivity and a second region of p-type conductivity with a junction therebetween, and

conductive contacts connected to said material for receiving a potential that forward biases said junction causing electrons to be emitted near said junction into an exterior region.

2. The device of claim 1 wherein said wide-bandgap material is diamond.

3. The device of claim 2 wherein said first region having n-type conductivity is carbon ion implanted diamond.

4. The device of claim 3 wherein said carbon ion implanted diamond is formed by carbon ion implantation into a diamond substrate heated to at least 320 °C.

5. The device of claim 4 wherein said carbon ion implantation is effected using a carbon ion current density of about 10^{-5} A cm^{-2}, with ion energies in the range of about 50 keV to about 170 keV, and fluences in the range of about 3.0×10^{16} cm^{-2} to about 3.8×10^{16} cm^{-2}.

6. The device of claim 2 wherein said second region having p-type conductivity is doped homoepitaxial diamond.

14. The method of claim 13 and further including the step of forming said junction in a diamond substrate.

15. The method of claim 14 wherein said step of forming a junction further comprises implanting carbon ions in said diamond, thereby forming said first region having n-type conductivity.

16. The method of claim 15 wherein said implanting further comprises heating said diamond substrate to at least 320 °C.

17. The method of claim 16 wherein said implanting further comprises using a carbon ion current density of about 10^{-5} A cm^{-2}, with ion energies in the range of about 50 keV to about 170 keV, and fluences in the range of about 3.0×10^{16} cm^{-2} to about 3.8×10^{16} cm^{-2}.

18. The method of claim 14 wherein said step of forming a junction further comprises doping homoepitaxial diamond thereby forming said second region having p-type conductivity.

19. The method of claim 18 wherein said doping further comprises forming said homoepitaxial diamond by chemical vapor deposition with boron concentrations up to 10^{19} cm^{-3}.

20. The method of claim 18 wherein said step of forming a junction further comprises forming said second region to be less than about 1 μm thick.

21. The method of claim 13 and further comprising placing conductive aluminum contacts on said material,

29. The method of claim 25 wherein said step of treating with gas includes delivering a gaseous plasma to said device near said junction.

30. The method of claim 29 wherein said step of treating with a gaseous plasma includes a gaseous plasma containing particles from the group consisting of O, H and OH.

31. A cold cathode device in accordance with claim 1 wherein said first region comprises diamond,

and further comprising a source of an electric potential connected to said conductive contacts establishing an electric field across said junction of less than 10^6 V cm^{-1}.

32. The device of claim 31 wherein said wide-bandgap material is formed with sharp points.

33. A cold cathode device in accordance with claim 32 wherein said sharp points are formed by ion-beam-assisted etching.

34. A cold cathode device in accordance with claim 2 and further comprising an emitting surface near said junction that is (111)-orientation of diamond.

35. A cold cathode device in accordance with claim 2 wherein said first region is formed with phosphorous doping.

36. A cold cathode device consisting of a large band gap material n-type, semiconductor from which electrons are emitted by an electric field of less than 10^6 V cm^{-1} in the space above the semiconductor surface.

ion implanting with a substantially 50 keV ion beam and a dose of substantially 3.2×10^{16} cm^{-2}.

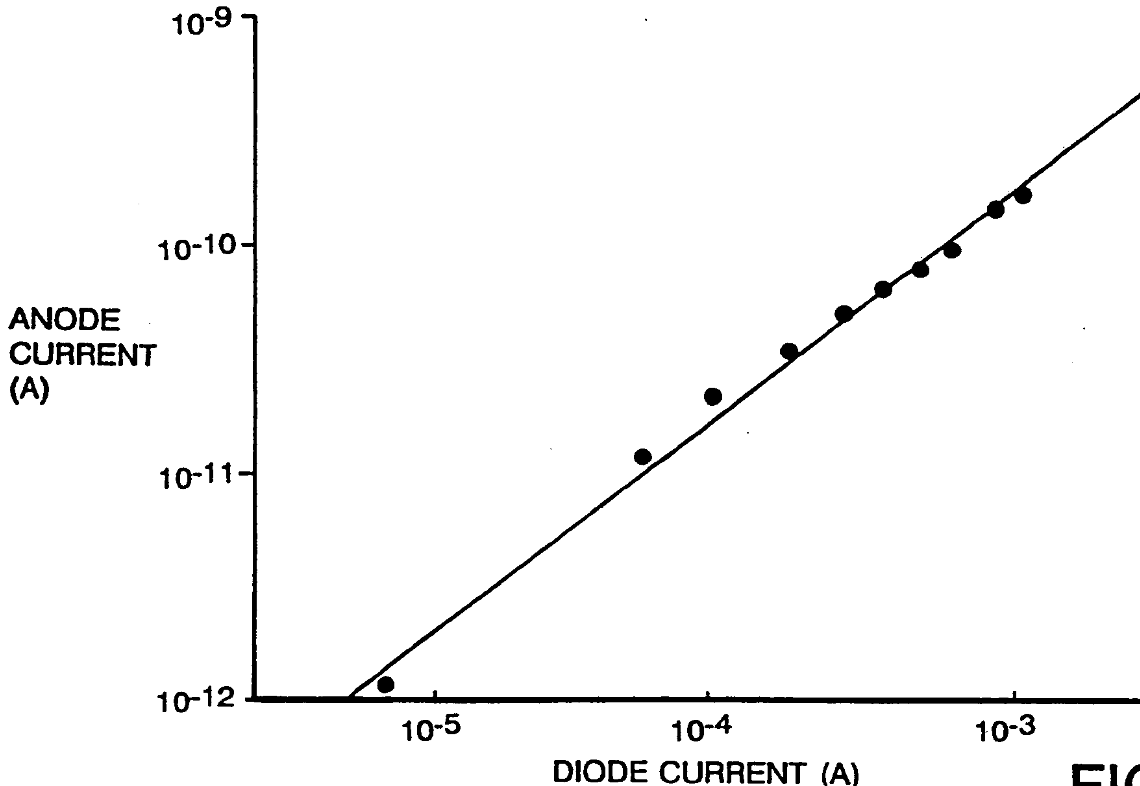
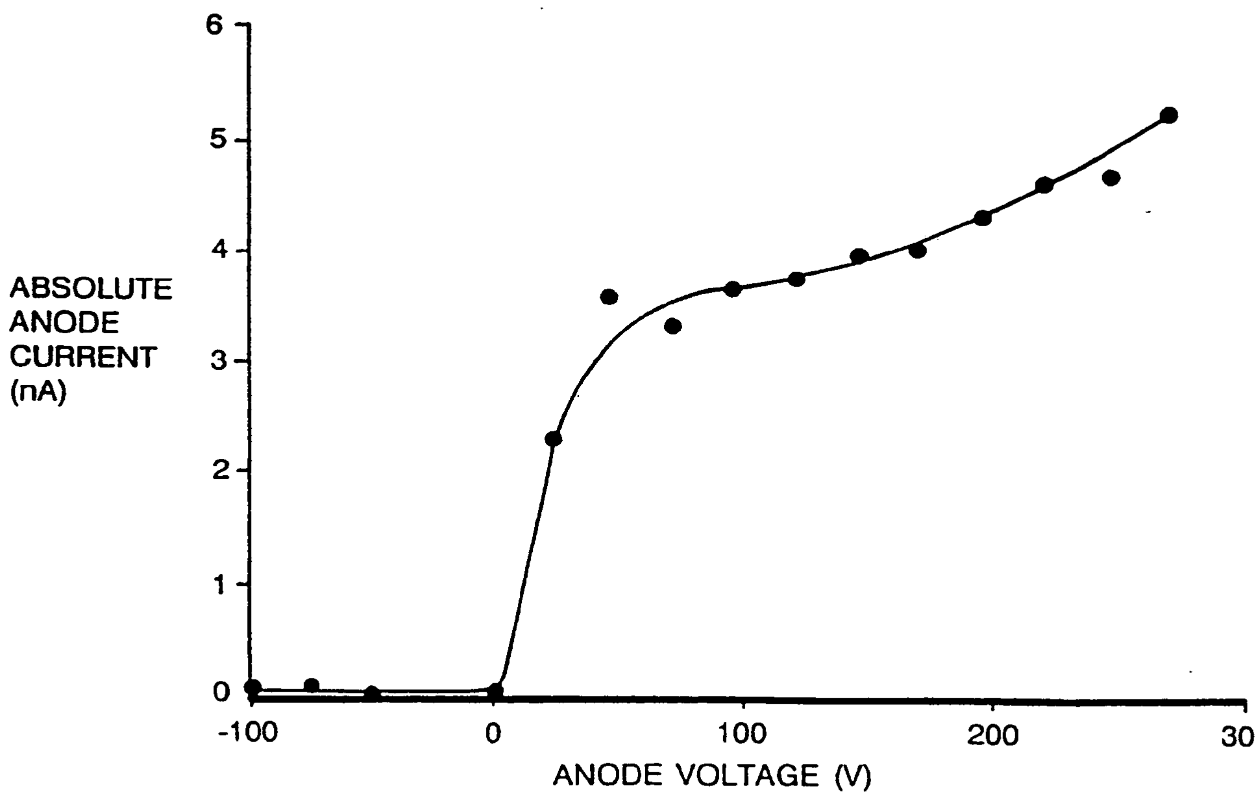


FIG. 3



SUBSTITUTE SHEET

FIG. 4

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,513,308 (GREENE ET AL.) 23 April 1985, See the cover figure.	32-33
Y	US, A, 4,506,284 (SHANNON) 19 March 1985, See figure 4.	11-12,23-24